Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 15 (2011) 4382 – 4386

Procedia Engineering

www.elsevier.com/locate/procedia

Advanced in Control Engineering and Information Science

Study on Thermoelectric Properties of Bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ Prepared by Sintering

Kegao Liu*, Nianjing Ji, Jing Li

School of Materials Science and Engineering, Shandong Jianzhu University, Fengming Road, Jinan 250101, China

Abstract

Bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ and $Ce_{0.9}Fe_3Co_1Sb_{12}$ were prepared by mechanical milling and sintering. The phases of the products were characterized by X-ray diffraction (XRD) and their thermoelectric properties were tested by electric constant instrument and laser thermal constant instrument. Experimental results show that, the major phases of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ and $Ce_{0.9}Fe_3Co_1Sb_{12}$ are skutterudite but the later has more purity phases. The electrical resistivities of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increase with temperature rising and are higher than those of $Ce_{0.9}Fe_3Co_1Sb_{12}$.The absolute values of α of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ are higher than those of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ and increase with temperature rising. The power factor of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increases with temperature rising at 100~500 ºC. The thermal conductivities of all $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ samples increase with temperature rising. ZT values of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ are all higher than those of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$. It obtains the maximum ZT value 0.2024 at 400 ºC.

Keywords: thermoelectric property; skutterudite; sintering

1. Introduction

Thermoelectric materials are the core parts of an thermoelectric apparatus, which enables to convert thermal energy to electric energy or vise versa. So the thermoelectric apparatus excels in clearness,

* Corresponding author: Kegao Liu. Tel.: +86-053186367285; fax: +86-053186367285.
E-mail address: liukg163@163.com

1877-7058 © 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.
doi:10.1016/j.proeng.2011.08.823

efficiency, long service life and reliability due to no moving parts and freon. Thus it can be applied in refrigeration or power industry and has broad prospect for application in many novel fields, such as micro-electronics, micro-machining and aviation-spaceflight. Therefore it paid more attention by many researchers[1~6]. The performance of thermoelectric materials is characterized by the dimensionless figure of merit, $ZT = (\alpha^2\sigma/\kappa)T$, where T is the temperature, α is the Seebeck coefficient (or named as thermoelectric power), σ and κ refer to the electric and thermal conductivity respectively. A satisfactory thermoelectric material should have low κ while high α and σ, and thus a high ZT value which simply indicates a high efficiency of thermoelectric conversion. The $CoSb_3$ type thermoelectric material with skutterudite structure is one of most promising thermoelectric materials [7]. Its thermoelectric properties can be adjusted in large extent by doping rare elements or by substituting Co or Sb atoms [8,9]. The preparation by mechanical milling and sintering and thermoelectric properties of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ were investigated in this work.

2. Experimental

The raw materials used in this work were: Iron, Cobalt powder (purity>99.5%, average granularity was 40.0 μm), Antimony powder (purity>99.5%，average granularity was 0.2~0.5 mm). Cerium powder (average granularity was 0.5mm) milled from a Ce bulk (purity>99.5%) in a glove box with Ar gas. Ce, Fe, Co and Sb powders were added in appropriate proportions to satisfy the molar ratios of $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$(x=1 and 3). Mechanical milling process was performed in a high-energy ball mill (working voltage was 110 V to make it keep in a certain rotating velocity); Steel balls with different diameters (Φ4～15 mm in a certain proportion) were encased into ball pot with Ar gas to prevent the powders from oxidation in milling. The weight ratio of the powders to balls was 20:1. Before the sintering started, the $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ powders were pressed into the graphite die (20 mm in diameter) and put into the sintering furnace, and then sintered at 650 ºC for 10 min. The system was evacuated to a pressure of 3 Pa, which was maintained till the sintering was completed. The dimension of the disc sample obtained via sintering was about Φ 20 mm×3.5 mm. The as-sintered samples were cut and polished into bars (3mm×3mm×18mm) for electrical property measurements, and some samples were machined into discs (Φ 10 mm×1 mm) for the tests of thermal properties. The phases of the sintered bulk samples were analyzed by X-ray diffraction (XRD). The densities of sintered samples were estimated via Archimedes method. Thermoelectric properties at different temperatures were tested by electric constant instrument and laser thermal constant instrument.

3. Results and discussion

3.1 Phases and densities of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

Fig.1 shows that the major phase of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ is skutterudite, but the phases of the other sample of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ are mainly skutterudite and obviously purity phases. Sintered bulk samples obtain high densities of 7.558 g/cm^3 and 7.382 g/cm^3 for bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ and $Ce_{0.9}Fe_1Co_3Sb_{12}$ respectively.

3.2 Electrical properties of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

Fig.2 shows that the electrical resistivities of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increase with temperature rising but those of $Ce_{0.9}Fe_3Co_1Sb_{12}$ have no obvious change with temperature rising. It shows that bulk $Ce_{0.9}Fe_1Co_3$

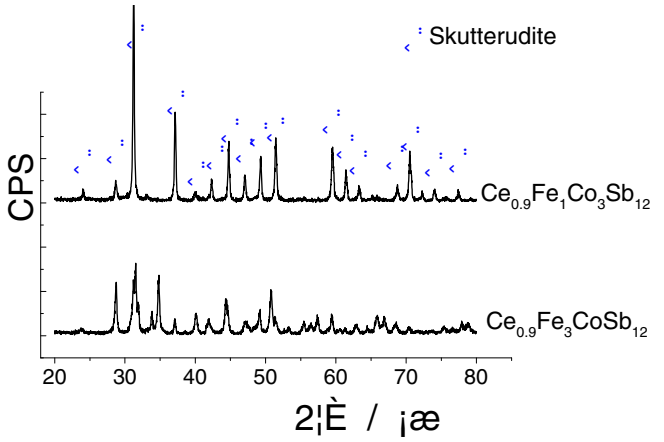

Fig.1 XRD patterns of the bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

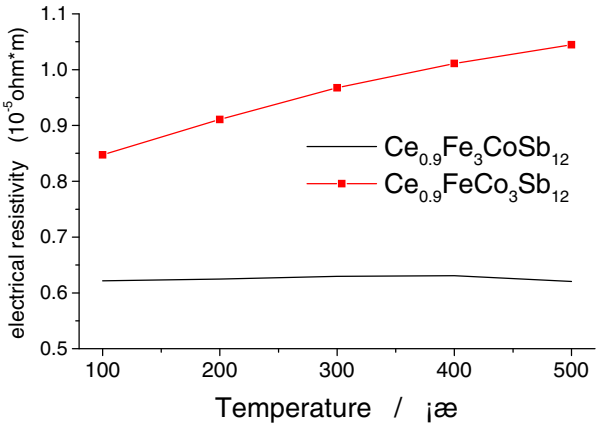

Fig.2 Electrical resistivities of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

-Sb_{12} has the characteristic of typical semiconductor electricity. It also indicates that the electrical resistivities of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ are higher than those of $Ce_{0.9}Fe_3Co_1Sb_{12}$.

Fig.3(a) shows temperature dependence of the Seebeck coefficients for bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$. The Seebeck coefficients (α) are negative $Ce_{0.9}Fe_1Co_3Sb_{12}$ at 100~500 ºC, which indicates the samples are N-type semiconductor materials, while those of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ are positive at 100~500 ºC, which indicates that the samples are P-type semiconductor materials. Due to the higher the absolute value of α the higher the *ZT* value according to the formula of *ZT*. It shows that the absolute values of α of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ are higher than those of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ and increase with temperature rising.

The power factor ($\alpha^2\sigma$) shows the total changes of the electrical properties. Fig.3(b) indicates that the power factors of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$. It can be seen that the power factor of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increases with temperature rising at 100~500 ºC and it shows no obvious temperature dependence at 100~500 ºC for bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$. Generally the power factor gets the maximum value at 500 ºC.

3.3 Thermal properties of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

Fig.4(a) shows the thermal conductivities of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$. It indicates that the thermal conductivities of all $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ samples increase with temperature rising. The maximum thermal conductivity value of $Ce_{0.9}Fe_1Co_3Sb_{12}$ and $Ce_{0.9}Fe_3Co_1Sb_{12}$ is up to 0.1399 $Wm^{-1}K^{-1}$ at 500 ºC.

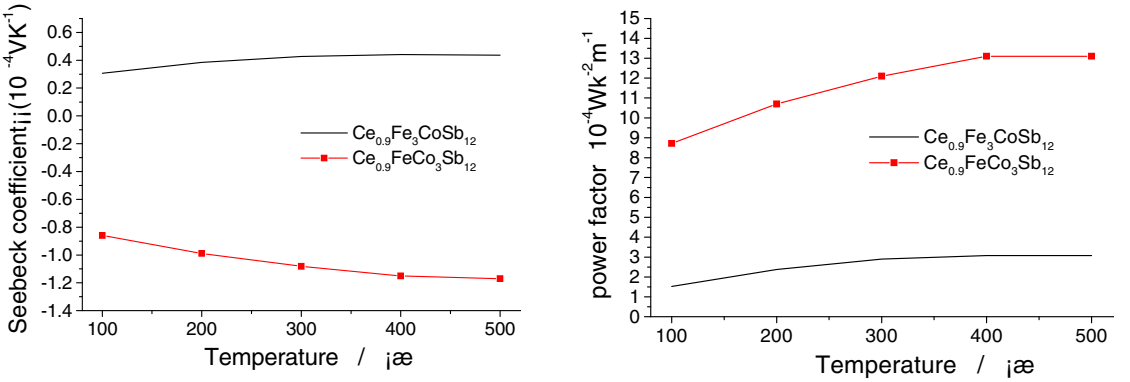

Fig.3 (a) Seebeck coefficients of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$; (b) Power factors of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

3.4 ZT values of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

Fig.4(b) shows ZT values of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$. It can be seen that the ZT value of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increases first at 100~400 ºC and then decreases at 400~500 ºC with temperature rising at 100 ºC, but for that of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ increases first at 100~300 ºC and then decreases at 300~500 ºC. ZT values of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ are all higher than those of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$. It obtains the maximum value 0.2024 at 400 ºC.

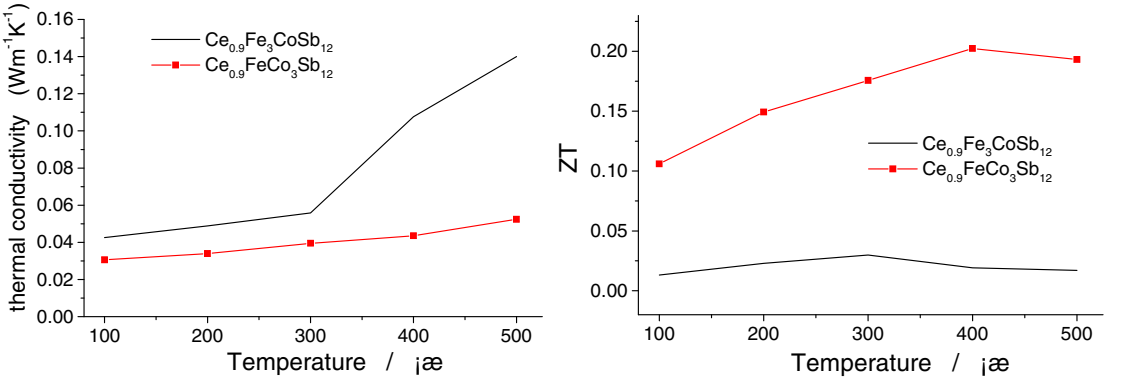

Fig.4 (a) Thermal conductivities of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$; (b) ZT values of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$

4. Conclusions

Bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ with x = 1 and 3 were prepared by mechanical milling and sintering at 650ºC under 30MPa. The major phase of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ is skutterudite, but the bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ has obviously purity phases. The electrical resistivities of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increase with temperature

rising. Bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ belongs to typical semiconductor. The $Ce_{0.9}Fe_1Co_3Sb_{12}$ samples are N-type semiconductor and while bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ samples are P-type semiconductor. The power factor of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increases with temperature rising at 100~500 ºC. The thermal conductivities of all $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ samples increase with temperature rising, the maximum value of $Ce_{0.9}Fe_1Co_3Sb_{12}$ and $Ce_{0.9}Fe_3Co_1Sb_{12}$ is up to 0.1399 $Wm^{-1}K^{-1}$ at 500 ºC. The ZT value of bulk $Ce_{0.9}Fe_1Co_3Sb_{12}$ increases first at 100~400 ºC and then decreases at 400~500 ºC with temperature rising at 100 ºC, but for that of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$ increases first at 100~300 ºC and then decreases at 300~500 ºC. ZT values of bulk $Ce_{0.9}Fe_xCo_{4-x}Sb_{12}$ are all higher than those of bulk $Ce_{0.9}Fe_3Co_1Sb_{12}$. It obtains the maximum value 0.2024 at 400 ºC.

Acknowledgement

This work was supported by the Shandong excellent middle-aged and young scientist encourage and reward foundation (No.2007BS04020) and the Project of Shandong Province Higher Educational Science and Technology Program (No.J11LD10).

References

[1] T.X Liu, X.F Tang, W.J. Xie. Journal of Rare Earths, Vol.25, Iss.6,(2007): 739-743.
[2] P. Vaqueiro, G.G. Sobany. Journal of Solid State Chemistry, Vol.179, Iss.7,(2006): 2047-2053.
[3] S.W. Kim, Y.Kimura. Science and Technology of Advanced Materials, Vol.5, Iss.4, (2004): 485-489.
[4] H.H. Saber, M.S. El-Genk, T. Caillat. Energy Conversion and Management, Vol.48, Iss.2, (2007): 555-567.
[5] J.Y. Yang, X.A. Fan. Journal of Alloys and Compounds, Vol.416, No.1-2, (2006) : 270-273
[6] J.L. Mi, X.B. Zhao. Journal of Alloys and Compounds, Vol.399, Iss.1-2,(2005): 260-263.
[7] B.C. Sales. Current Opinion in Solid State & Mater. Sci. (1997), No.2: 284-289.
[8] T.X.Liu, X.F.Tang, W.J. Xie. Journal of Rare Earths, Vol.25, No.6, (2007): 739-743.
[9] N. Ogita, T. Kondo: Physica B. Condensed Matter, Vol.383, No.1, (2006): 128-129
[10] P.X. Lu, F. Wu. Journal of Alloys and Compounds, Vol.505, Iss.1,(2010): 55-258.